QUALITY ASSURANCE PROJECT PLAN
FOR
REAL-TIME MONITORING OF ORGANIC CARBON IN THE DELTA

August 1, 2001

California Department of Water Resources
Division of Planning and Local Assistance
Municipal Water Quality Investigations Program
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3. Distribution List

The following individuals and organizations have received copies of the approved Quality Assurance Project Plan (QAPP):

Phil Wendt	Department of Water Resources
Dan Otis	Department of Water Resources
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Richard Woodard	State Water Contractors

4. Project Organization

The Real-time Monitoring of Organic Carbon in the Delta Project (RTMC Project) is a CALFED/EPA funded program that is being conducted by the Department of Water Resources (DWR), Municipal Water Quality Investigations Unit (MWQI). Table 1 lists the key DWR personnel responsible for the RTMC Project.

Table 1. Project Organization Structure

Title/Responsibility	Name	Phone Number
Project Managers	Jim Sickman	(916) 327-1724
	David Gonzalez	(916) 371-3163
Staff	Lori Weisser	(916) 445-9843
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5. Problem Identification/Background

Waters of the Sacramento-San Joaquin Delta serve nearly 23 million people living in the Bay-Delta region and in southern California. Therefore maintaining good water quality in the Delta is important to public health and the economy of the State.

Total organic Carbon (TOC) and dissolved organic carbon (DOC) in Delta waters are growing concerns for drinking water quality. TOC and DOC are disinfection by-product (DBP) precursors which can form carcinogenic compounds (such as trihalomethanes and haloacetic acids) during disinfection processes; federal regulations are pending to limit DOC/TOC levels in water supplies for drinking water. Given the complexity of the carbon cycle in the Delta, estimating the sources and loads of DOC/TOC is difficult and more information is needed to assess the relative carbon contributions from riverine inputs and in-Delta sources. DWR scientists are attempting to model DOC transport and fate in the Delta, to predict the water quality effects of changes in Delta management practices promulgated by the CALFED program.

TOC originates from a wide variety of sources incident to and within the Delta including both natural and anthropogenic sources:

? Agricultural drainage (including Delta island runoff)
? Wetlands
? Riparian vegetation
? Algae
? Upland and urban runoff
? Wastewater treatment plants

DOC/TOC data typically have been collected as grab samples for laboratory analysis on a weekly or monthly basis. This frequency of data has proven to be of limited value in establishing baseline water quality conditions, in assessing the sources and loads of DOC/TOC in the system and in developing simulation models to predict carbon movement and concentration in the Delta. CALFED identified a need for monitoring DOC/TOC in a real-time network with sufficient accuracy to identify changes in sources and loadings that result from CALFED actions designed to improve drinking water quality, restore ecosystems and increase water storage.

The RTMC Project will develop and implement a monitoring system that can be used to address key data gaps for three broad information needs: (1) baseline water quality conditions in source waters and diverted drinking water supplies; (2) carbon loading from the Sacramento and San Joaquin Rivers; and, (3) assessment of continuous water quality improvement during the first phase of CALFED. Furthermore, this project is the first step towards developing an early-warning/forecasting system for critical water quality constituents in the SWP. The RTMC Project will measure the concentrations of DOC/TOC flowing into the Delta from the two largest sources—the Sacramento and San Joaquin Rivers—and at the headworks of the SWP. These data will be used by CALFED managers to assess the impacts of management decisions on TOC loads within the Delta and SWP. Data on TOC levels will also be made available to the State Water Contractors (SWCs) on a real-time basis as an aid to water treatment and blending activities. DWR modelers will utilize the data to help parameterize and validate a carbon simulation model currently being developed.

6. Project Description

Real-time monitoring of organic carbon (DOC/TOC) has not been conducted in the Delta in the past. The primary objective of this project is to determine the feasibility of establishing field stations for continuous monitoring of surface water DOC/TOC levels. The major tasks of the project are:

(1) Evaluate current analytical methods and instruments for DOC/TOC analysis
(2) Install and operate DOC/TOC autoanalyzers at field locations
(3) Evaluate the accuracy of the data generated by the field instruments
(4) Determine if long-term operation of these autoanalyzers is logistically feasible and cost-effective
(5) Evaluate and install a data telemetry/remote control system to provide real-time access to DOC/TOC data and allow for remote operation of the autoanalyzers

When completed, this project will provide real-time data on carbon levels in the Sacramento River, San Joaquin River and headworks of the State Water Project. If the project is successful, similar real-time DOC/TOC stations could be installed at other key locations throughout the Delta and at Delta export locations (Delta Mendota Canal, North Bay Aqueduct etc.).

To measure organic carbon in surface waters, complex organic molecules must be first broken down and converted into a single-carbon molecular form (either CO_2 or methane) which can be directly detected. Currently there are three methods for determining the DOC/TOC levels in water: the combustion-infrared method; the persulfate-ultraviolet oxidation method; and the wet-oxidation method. Of the three techniques, wet oxidation is the least commonly used and is not appropriate for TOC measurements. Thus, only the combustion and combination methods will be evaluated in the RTMC Project. Criteria used to evaluate the DOC/TOC autoanalyzers include: (1) the ability to operate in an unattended autosampling mode, (2) have telemetry/remote-control capabilities, (3) the ability to produce laboratory-quality DOC/TOC measurements under different water flow and turbidity regimes. Once a decision has been made regarding the most appropriate analytical method and autoanalyzer, three analyzers will be purchased and installed in the field. Installation will be completed sequentially rather than simultaneously to allow us to refine instrument operation and maintenance protocols and transfer this knowledge from one installation to the next.

Organic carbon autoanalyzers will be installed at the following Sacramento-San Joaquin Delta locations: (1) on the Sacramento River at the Hood Field Station, (2) on the San Joaquin River at the Vernalis station and (3) at Harvey O. Banks Pumping Plant at Byron, California. Water quality stations have already been established at Banks and Hood by DWR Environmental Services Office and Division of Operations and Maintenance

Figure 1. Banks (L) and Hood (R) Stations

(Figure 1) and the DOC/TOC analyzers will be installed in these existing instrument shelters. However, there is no similar infrastructure at the Vernalis site, so a walkway and instrument shelter will need to be built prior to installation of the autoanalyzer. Data telemetry/remote-control options will be evaluated and then implemented. Once this system is in place, real-time DOC/TOC data will be published on the Internet for use by CALFED scientists, SWCs staff and DWR modelers.

6.1 Current Project Status

The RTMC project was initiated in 1999 with funding from CALFED, EPA and the SWCs. Several DOC/TOC methods and analyzers were evaluated for their suitability to measure carbon in Delta waters. A Sievers Model 800 organic carbon autoanalyzer was installed at the Hood station in June 1999. This autoanalyzer measures carbon using a variation of the persulfate-ultraviolet method. Testing of the Sievers unit has shown that, while the instrument is reliable and easy to maintain, it is suitable only for DOC measurement. During periods of high water turbidity, TOC values were consistently under-estimated. Other comparisons between combustion and non combustion methods for carbon analysis (EPA Method 415.1 and 415.2) have shown that recovery of particulate organic carbon (POC) using persulfate-ultraviolet oxidation or wet-oxidation can be poor, thus causing under-estimation of TOC. Measurement of organic carbon by combustion techniques, are generally more suitable to samples with higher POC content and are the best available method for measuring carbon concentrations in the Delta. Because a primary objective of RTMC Project is TOC, the Sievers unit is scheduled for replacement with a combustion autoanalyzer capable of accurate measurement of both TOC and DOC (see Section 6.2).

As of June 2001, instrument evaluation has been completed and 3 Shimadzu 4100 DOC/TOC autoanalyzers have been purchased. The Shimadzu TOC 4100 is a high performance on-line TOC autoanalyzer using the established 680°C catalytic combustion and non-dispersive infrared detection method. One of the units was installed at the Banks Pumping Plant in February 2001 and has been undergoing testing for the past six months (Figure 2). The instrument has worked well and has been quite reliable and appears to be suitable for continuous, field use.

Figure 2. Shimadzu TOC 4100 Carbon Autoanalyzer at Banks Station

MWQI staff have identified a suitable site for the Vernalis RTMC Project station and a preliminary cost estimate has been obtained from a licensed contractor. The station will be built on an existing levee approximately 0.25 miles downstream of the Vernalis bridge and will consist of an instrument shelter and walkway.

6.2 Tasks for 2001-2003

Banks and Hood Stations

During 2001-2003 MWQI staff will make the Banks DOC/TOC station fully operational and install a second DOC/TOC station at Hood. Since the RTCM project is a feasibility study, protocols for routine operation and maintenance of the Shimadzu analyzers will be continually refined during the next two years. Several operational and quality control tasks remain to be completed at the Banks station before replacement of the Sievers unit at Hood Station. These tasks include upgrades to the water delivery system, an assessment of data telemetry options, installation of a data telemetry system and design and deployment of an Internet interface to allow end-users real-time access to DOC/TOC database. The RTMC autoanalyzer will be included in round-robin studies involving Bryte Laboratory and other certified analytical laboratories. These interlaboratory comparisons of field and laboratory DOC/TOC measurements will be evaluated and QA/QC reports will be produced in 2002. A final report evaluating the feasibility of real-time monitoring of DOC/TOC at the Banks and Hood stations will be completed in 2003. These and other uncompleted project elements are described in Table 2.

Table 2. RTMC Project Tasks for the Banks and Hood Stations: 2001-2003

Projected Timeline for the RTMC Project 2001-2003	J-01	A-01	S-01	O-01	N-01	D-01	J-02	F-02	M-02	A-02	M-02	J-02	J-02	A-02	S-02	O-02	N-02	D-02	J-03	F-03	M-03	A-03	M-03	J-03
Banks Real-time Carbon Station																								
Biweekly Site Visit	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Hourly TOC measurement	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Upgrade water delivery system	X	X																						
Hourly DOC measurement			X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Investigate data telemetry options	X	X	X	X																				
Install data telemetry system					X																			
Internet publishing of Real-time Carbon data				X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Interlaboratory Comparison (see Section 7)	X	X	X	X	X																			
Interlaboratory Comparison Report						X																		
Hood Real-time Carbon Station																								
Biweekly Site Visit: Hood	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Hourly DOC measurement	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Install Shimadzu 4100 TOC/DOC analyzer								X																
Upgrade water delivery system					X	X																		
Hourly TOC measurement								X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Install data telemetry system								X																
Internet publishing of Real-time Carbon data								X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Interlaboratory Comparison (see Section 7)								X	X	X	X	X												
Interlaboratory Comparison Report													X											
Final Report on Real-time TOC Feasibility																								X

Vernalis Station

Construction of the Vernalis station is contingent upon additional funding from the CALFED Drinking Water Quality Program. A proposal was submitted on July 3, 2001 and included a request for money to construct the instrument shelter and walkway, and install a water delivery system and multi-parameter monitoring station (parameters include pH, conductivity, turbidity, temperature and dissolved oxygen). Once funding is secured and the station infrastructure built, the DOC/TOC autoanalyzer will be installed. A tentative timeline for the Vernalis station is shown in Table 3.

Table 3. RTMC Project Tasks for the Vernalis Station: 2001-2003

Projected Timeline for the RTMC Project 2001-2003	J-01	A-01	S-01	O-01	N-01	D-01	J-02	F-02	M-02	A-02	M-02	J-02	J-02	A-02	S-02	O-02	N-02	D-02	J-03	F-03	M-03	A-03	M-03	J-03
Vernalis Real-time Carbon Station																								
Site survey	X	X																						
Solicitation of additional CALFED funding	X																							
Engineering design of station					X	X																		
Acquisition of permits							X	X	X															
Solicitation of construction bids										X	X													
Award construction contract												X												
Construction of shelter and walkway													X	X	X									
Installation of water delivery system															X									
Installation of multiparameter sensor																X								
Installation of TOC/DOC analyzer																X								
Biweekly Site Visit																	X	X	X	X	X	X	X	X
Hourly TOC/DOC measurement																	X	X	X	X	X	X	X	X
Install data telemetry system																	X							
Internet publishing of Real-time Carbon data																		X	X	X	X	X	X	X
Interlaboratory Comparison (see Section 7)																		X	X	X	X	X		
Interlaboratory Comparison Report																								X

7. Data Quality Objectives for Measurement Data

The Shimadzu autoanalyzer is a laboratory instrument that has been modified for field installation and continuous monitoring of DOC/TOC in water treatment plants, rivers and industrial settings. MWQI staff have utilized the manufacturer's technical assistance during instrument installation and calibration to maximize performance of the autoanalyzer. Our overall data quality objective is to produce hourly DOC/TOC measurements of the same precision and accuracy as grab samples analyzed in the laboratory. To do this we will make regular comparisons of autoanalyzer and laboratory DOC/TOC measurements (see Sections 10-14 for further details).

Laboratory DOC/TOC analyses will be performed at DWR's Bryte Chemical Laboratory in West Sacramento. This state of the art laboratory provides analytical, chemical and biological services for DWR and other governmental agencies. The laboratory's Quality Assurance Manual is appended to this QAPP and provides detailed information on Bryte Laboratory's Quality Assurance Program including laboratory organization, sample procedures, instrument calibration and maintenance, analytical methods, quality control procedures and reporting requirements. All activities conducted as part of the RTMC will adhere to the protocol listed in this Quality Assurance Program (see Appendix I).

7.1 Precision and Accuracy

Precision and accuracy goals for DOC/TOC measurements by the Shimadzu 4100 field unit and at Bryte laboratory using grab samples are summarized in Table 4. Accuracy will be assessed by analyzing standard reference materials (SRM) composed of both synthetic and natural waters. Precision will be assessed by analyzing replicate samples of synthetic standards and natural waters. Intercomparisons of field and laboratory DOC/TOC measurements and determinations of precision and accuracy will be made throughout the year for different source-water qualities to account for matrix effects.

Table 4. Data Quality Objectives for Field and Laboratory DOC/TOC Measurements

Parameter	Detection Limit	Reporting Limit	Accuracy Objective	Accuracy Protocol	Precision Objective	Precision Protocol
Autoanalyzer TOC (EPA 415.1)	0.1 mg/L	0.5 mg/L	80-120%	SRM	30%	RPD of Replicates
Autoanalyzer DOC (EPA 415.1)	0.1 mg/L	0.5 mg/L	80-120%	SRM	30%	RPD of Replicates
Lab TOC (EPA 415.1)	0.1 mg/L	0.5 mg/L	80-120%	SRM	30%	RPD of Replicates
Lab DOC (EPA 415.1)	0.1 mg/L	0.5 mg/L	80-120%	SRM	30%	RPD of Replicates

7.2 Comparability

In addition to the intercomparison between the field and laboratory DOC/TOC measurements, we will send duplicate grab samples to outside laboratories monthly for carbon analysis by the combustion method. Data from these round-robin interlaboratory comparisons will be included in the 2002 QA/QC reports.

7.3 Completeness

The primary purpose of the RTMC project is to test the feasibility of installing and operating real-time DOC/TOC stations. There are currently no legal compliance uses for the DOC/TOC data and there is no fraction of the planned data that must be collected in order to fulfill statistical criteria. For the purposes of the feasibility study we have established the following goals for data completeness: (1) data capture of at least 50% during any one month and (2) data capture of at least 75% during any yearly period. For QA/QC analyses, at least 2 interlaboratory comparison samples will be collected and analyzed monthly for a period of 5-6 months. An interlaboratory report will be written for each station once a minimum of 15 interlaboratory samples have been analyzed.

7.4 Representativeness

Grab samples of river and aqueduct water will be collected across the full width of the channels under different hydrologic conditions to assess horizontal and vertical variations in DOC/TOC concentrations and determine the representativeness of the water intakes at the RTMC stations. Hydrologic regimes that will be sampled include winter storm runoff and summer low flows. Samples will also be taken at the water system inlet and outlet and analyzed to assess whether carbon is lost or gained in the water delivery system (i.e., pumps, PVC pipe and plastic tubing). Results from these investigations will be included in the Real-time DOC/TOC Final Report.

8. Training Requirements/Certifications

A service contract has been purchased for each Shimadzu DOC/TOC autoanalyzer which includes factory training on instrument installation and operations. All instrument operators have received this training and have on-site access to technical documentation for the autoanalyzers, including standard operating procedures (SOPs). All personnel will have a working knowledge of the QA Project Plan and ensure that all work is in compliance with the QAPP and is performed according to written SOPs (Appendix 2). Field staff will also ensure that all documentation is complete and accurate.

9. Documentation and Records

The Shimadzu autoanalyzer produces a computer printout of each analysis, along with all calibration data, and sample date and time. The calibration printout includes date and time, standards identification, injection amount and calculated coefficient value. The printouts are kept at the MWQI Field Office. In addition, all data is downloaded from the sampling unit using a Campbell Scientific datalogger and stored in an Excel spreadsheet at the MWQI Field Office and in the MWQI Field and Laboratory Information Management System (FLIMS) database.

On each site visit to collect grab samples for QA/QC analysis, sampling team identification, site identification, sample identification number, date and time sample will be recorded on a pre-printed field sheet. The form will also record the type of container and preservation methods used, and any other pertinent information for the grab samples. The original field sheet will be kept at the MWQI Field Office and copies given to the laboratory at the time the samples are transferred to the laboratory. All laboratory data will be stored in the DWR FLIMS database, which is operated and maintained by the DWR Bryte Laboratory.

10. Sampling Process Design

The Shimadzu autoanalyzer will perform DOC/TOC analyses every hour, seven days per week, 365 days per year. Each set of analyses is a series of five samples collected and analyzed within a 20-minute period at the top of each hour. Additionally, grab samples will be collected on a weekly basis for QA/QC requirements. When the RTMC project is fully functional samples will be collected at Banks Pumping Plant, Hood Station on the Sacramento River and at Vernalis on the San Joaquin River.

During each grab sample event, several QA/QC samples will be taken including a deionized water sample carried into the field as a bottle blank (Table 5); these samples will be returned to the Bryte Laboratory and analyzed for TOC and DOC.

Table 5. Sampling Design for Autoanalyzer QA/QC Measurements

Parameter	Number of Samples Collected
QA/QC for DOC (0.45 ? m)	Duplicate grab samples will be collected during hourly automated analyses to be returned to Bryte laboratory for analysis or to be used in the round-robin QA/QC study. AND One certified DOC sample will be analyzed (in triplicate) on the Shimadzu 4100 field for determination of precision and accuracy
QA/QC for TOC (unfiltered)	Duplicate grab samples will be collected during hourly automated analyses to be returned to Bryte laboratory for analysis or to be used in the round-robin QA/QC study. AND One certified TOC sample will be analyzed (in triplicate) on the Shimadzu 4100 field for determination of precision and accuracy
Water System Evaluation: DOC 1. Water System Inlet 2. Autoanalyzer Inlet 3. River/Canal	One grab sample at each of 3 sampling points to be returned to laboratory for analysis to assess water system contamination
Water System Evaluation: TOC 1. Water System Inlet 2. Autoanalyzer Inlet 3. River/Canal	One grab sample at each of 3 sampling points to be returned to laboratory for analysis to assess water system contamination
Bottle Blank (DOC) filtered	One bottle of deionized water carried into the field and then returned to the Bryte Laboratory of DOC analysis. Used to assess bottle contamination (QA/QC)

11. Sampling Methods Requirements

Surface water sampling will be limited to grab samples used for QA/QC procedures (Table 5). Both DOC and TOC grab samples will be collected during automated analyses and brought back to the Bryte Laboratory or used in the round-robin interlaboratory comparison. Grab samples will be collected in cleaned, acidified (H_3PO_4) 40-ml clear glass vials. No other preservatives are required for these samples. The samples will be chilled to 4?C immediately upon collection. The containers are pre-cleaned and acidified (H_3PO_4) and will not be rinsed prior to sample collection. Table 6 contains a summary of the sampling methods to used in the RTMC project.

Table 6. Parameter Table for Field and Laboratory DOC/TOC Measurements

Parameter	Number of Samples	Matrix	Sample Preservation	Sample Container	Holding Time
Shimadzu Autoanalyzer: DOC<0.45? TOC>0.45?	Perform 5 analyses hourly seven days per week	Surface water	Field analyses; no samples taken	N/A	N/A
Lab Grab Samples: Unfiltered TOC Field Filtered DOC (<0.45?)	One each at water system and autoanalyzer inlet, and in river or aqueduct AND Duplicate grab samples will be collected during hourly automated analysis	Surface water	Acid preserved (H_3PO_4), store at 4?C	Screw-top Clear glass	14 days

12. Sample Handling and Custody Requirements

All samples will be collected and handled in a manner consistent with protocol established in the MWQI Field Manual except where changes are necessitated by this project (Appendix 1).

All DOC and TOC samples will be received by the DWR Bryte Laboratory (located in West Sacramento) following standard chain of custody procedures (Appendix 1). The collection bottles will be marked by MWQI field staff with a code number relating to the analysis requested. The laboratory will follow established protocols for analyzing these samples (see Appendix 1).

13. Analytical Methods Requirements

The catalytic combustion method will be used for DOC/TOC analyses at the field stations, Bryte Laboratory and during the round-robin interlaboratory comparison (EPA 415.1). At the field stations analyses will be done on a Shimadzu Model 4100 on-line TOC

Autoanalyzer using catalytic combustion and infrared detection. In the autoanalyzer, inorganic carbon is removed by acidification and purging hence the instrument measures non-purgeable organic carbon (NPOC) on both filtered and unfiltered waters. The Bryte Laboratory uses an O-I Corporation Model 1020A Combustion Total Organic Carbon Analyzer and employs similar combustion, detection and sample preparation techniques.

14. Quality Control Requirements

Precision and accuracy of autoanalyzer and laboratory analyses of DOC/TOC will be assessed for all RTMC stations. Autoanalyzer precision will be determined using triplicate measurements of both certified standards and natural waters. All grab samples for laboratory DOC/TOC analysis will be done in duplicate to assess the precision of the laboratory analyzer. Accuracy of both field and laboratory measurements will be assessed using standard reference materials made from synthetic standards and natural waters. Precision and accuracy determinations will be done on a twice-monthly basis at the field stations and during each analytical run at Bryte Laboratory. If QC samples fall out of desired control limits (see Table 4), the data will be flagged in the database.

To check for absorption/desorption of organic carbon in the water supply system we will compare DOC/TOC levels in grab samples collected near the intake of the water system Shimadzu autoanalyzer inlet port and in the aqueduct or river. To insure the comparability of field and laboratory DOC/TOC measurements we will, on a biweekly basis, collect grab samples at the Shimadzu inlet port when samples are being analyzed that will be run at the Bryte Laboratory and at other contract labs that are part of the round-robin interlaboratory comparison.

15. Instrument/Equipment Testing, Inspection, and Maintenance Requirements

The Shimadzu 4100 TOC Autoanalyzer will be thoroughly inspected and calibrated on each routine site inspection. Standard operating guidelines are contained in Appendix 2. Standards and deionized water blanks will be replaced biweekly; replacement intervals for other expendable components are listed in Appendix 2. In addition to information gathered on site visits, two warning conditions are recorded on the Campbell Datalogger and indicate whether the instrument is experiencing minor (Warning 1) or major (Warning 2) operating problems. Either warning level will trigger a visit to the site for evaluation and correction of the problem.

The laboratory TOC analyzer is tested, inspected and maintained by the Bryte Laboratory following guidelines found in their Quality Assurance Manual (see Appendix 1).

16. Instrument Calibration and Frequency

The Shimadzu TOC Autoanalyzer is automatically calibrated four times per day using a two point calibration procedure. Standards are 0 and 10 mg L^{-1} C and are prepared by the Bryte Laboratory using NIST-Traceable Standard Reference Materials. Baseline adjustment to the autoanalyzer will be made on each site visit (see Appendix 2). Calibration results are recorded on the instrument print-out and recorded on the Campbell Datalogger. Calibration results will be placed as metadata in the database. In addition, calibration can be remotely initiated at anytime using control ports on the Campbell Datalogger and the control software. Calibration results will be placed as metadata in the FLIMS database.

The laboratory TOC analyzer is calibrated by the Bryte Laboratory using NIST-Traceable Standard Reference Materials following guidelines found in their Quality Assurance Manual (see Appendix 1). These calibration results will also be placed as metadata in the database.

17. Inspection/Acceptance Requirements for Supplies

All expendable supplies (acids, CO_2 scrubbers etc.) will be purchased from Shimadzu Inc. and have undergone rigorous inspection at the factory. The deionized water and standards used for calibration of the field instrument will be prepared by the Bryte Laboratory and analyzed on the laboratory TOC analyzer to insure their quality.

18. Data Acquisition Requirements

All data used for the RTMC project will be obtained through our monitoring activities and no outside data sources will be required.

19. Data Management

19.1 Grab Sample Data

Before grab samples are collected, a sampling request is entered into the FLIMS database maintained by the Bryte Laboratory. All pertinent information about the samples to be collected (site, date, type of analyses requested, required sampling container, sampling protocol etc.) are required and FLIMS generates all of the field forms and bottle labels including unique sample code numbers. These forms along with the labeled bottles are taken into the field and the samples collected using established protocols. Next the grab samples are returned to the Bryte Laboratory where they are submitted to the laboratory auditor who verifies the chain of custody and records any changes in sampling information in the database. Once the samples enter the Bryte Laboratory they are tracked through all analytical procedures and this information is recorded in the FLIMS database.

19.2 Telemetered Data

Once a day, data will be downloaded remotely from the Campbell Datalogger using communication software and a modem. The data will automatically reviewed for initial data quality (relative standard deviation of replicate measurements, calibration quality, blank values etc.) using a programming script and placed into the FLIMS database as provisional data. Print-outs of analytical results will be collected on site visits and manually entered into the database. The data from the datalogger and printouts will be compared to insure there were no discrepancies; this comparison is done to insure that autoanalyzer output was accurately recorded on the datalogger. Data will be made official only after instrument performance has been validated by comparing field autoanalyzer results to values obtained from the weekly grab samples. We anticipate a delay of 1-2 weeks before data are finalized in the database.

20. Assessment and Response Actions

Field and laboratory DOC/TOC analyses, QA/QC results, calibration parameters and field notes will be reviewed on a weekly basis by the Project Managers (Sickman and Gonzalez) and the Quality Assurance Manager (Ngatia) to insure that all data quality objectives are being met (see Section 7 and Table 4). Interlaboratory comparisons will be conducted in the first 5-6 months after field stations are established and at least once a year thereafter to insure data quality. If problems are detected, the project Managers will consult with field staff and instrument manufacturers to rectify the situation. Corrective actions could include more frequent site service, more frequent instrument calibration or other actions deemed necessary.

21. Reports

Within 5-6 months of initial installation an Interlaboratory Comparison Report (ICR) will be prepared that will summarize all QA/QC data collected during initial station setup. This report will be prepared by the Project Managers (Sickman and Gonzalez) with assistance from the Quality Control Manager (Ngatia). After an ICR is prepared, quarterly summaries of real-time DOC/TOC data and QA/QC data will be produced by the Project Managers and published on the MWQI web page. Quarterly data reports will be forwarded to EPA, CALFED, SWC and other interested parties if requested.

A final report on the feasibility of real-time measurement of DOC/TOC using remote instrumentation will be produced by June 2003 by the project managers and published as an official DWR Water Quality Investigation Report. Copies will be sent to EPA, CALFED, SWCs and other interested parties.

22. Data Review, Validation, and Verification Requirements

Field and laboratory DOC/TOC analyses, QA/QC results, calibration parameters and field notes will be obtained from the FLIMS database and reviewed on a weekly basis by the Project Managers (Sickman and Gonzalez) and the Quality Assurance Manager (Ngatia) to insure that all data quality objectives are being met (see Section 7 and Table 4). Decisions to reject or qualify data will be made by the Project Managers.

23. Validation and Verification Methods

All QA/QC, real-time and laboratory DOC/TOC data and calibration results will be reviewed by the Project Managers (Sickman and Gonzalez) and the Quality Assurance Manager (Ngatia). Any real-time or laboratory DOC/TOC measurements that fall outside of the QA/QC ranges identified in Table 4 and Section 7 will be flagged in the database. Obvious outliers will be deleted and the average of measurements made immediately proceeding and after the bad data point will be substituted; this substitution will be noted in the database. Data recorded on the Campbell Datalogger will be manually compared to measurements recorded on the instrument printout. If recording errors are detected the problem will be isolated and corrected and the values from the printout will be included in the finalized data. However, only the datalogger output will go into the finalized FLIMS and MWQI datasets if no errors are detected; this protocol will minimize the potential for typographical errors in final data products and reports. All problems with interim and final data products will be noted in the FLIMS database and in all quarterly and final reports.

24. Reconciliation with Data Quality Objectives

Several times per month all QA/QC parameters will be computed (field and laboratory precision and interlaboratory comparison results) and corrective actions taken if necessary. If data quality indicators do not meet criteria stated in Section 7 and Table 4, then values will be flagged in the database or discarded. The cause of failure will be evaluated and corrective measures implemented. If the cause is instrument failure then site visits and instrument calibration intervals will be reassessed and improved. If problems are caused by field or laboratory personnel then team members will be retrained. Any limitations on data use will be recorded in the FLIMS database as metadata and notations will be made in all quarterly data reports. Detailed assessments of all Data Quality problems will be discussed in the final Report.

Appendix 2
Real-time Monitoring of Organic Carbon Project
Standard Operations Guidelines

1.Shimadzu Model 4100 Testing, Inspection and Maintenance

1.1 Weekly Site Visit

1. Upon arriving, check the instrument printout. Make sure the autoanalyzer has been working by looking at the date and times of the records. Also, look for any abnormal spikes and dips in readings. These could be signs of other problems, such as clogged flows (very low numbers) and delivery system slough-off (high spikes).
2. Check flows at flow meter. System flow rates will very likely drop-off over time. Cycle the flow meter valve open and closed a few times to clear algae and other large particles from the flow meter valve assembly. Try to reset flow to around 3-liters per minute.
3. The next step is to check the baseline for the carrier gas. Press the enter key on the autoanalyzer keyboard to activate the screen. Next, look at the bottom of the screen for a menu tab. Press the associated F-4 key to get to the main menu. Scan down the list of headings to "Monitor" using the arrow keys and press enter. The screen that appears will have a graph which has a y-axis labeled in percent. If the scrolling cursor line is off zero percent an adjustment will need to be made. To make the adjustment open the front of the unit and look to the far right of the halogen scrubber. There should be a round mechanism with a protruding cylinder facing toward the front of the autoanalyzer. Inside of the cylinder is a standard screw head fitting. With a flat head screwdriver turn the screw clockwise to lower the baseline and counter-clockwise to raise it.

   ATTENTION: There are two screw holes in this vicinity. If you turn the wrong one serious damage will result. Therefore, if you are uncertain which is the correct screw ask someone who knows prior to completing this step.
4. Check the inside of the unit for problems. Check the following items:
   - ? main carrier gas gauge ~ 100-200kpa
   - ? carrier gas flow meter ~ 150mL/min
   - ? sparge gas flow meter ~ 150mL/min
   - ? gas generator pressure (on stand next to Shimadzu) ~ 90 psi
   - ? halogen scrubber, look for discoloration - replace if necessary
   - ? check expiration dates on soda lime scrubbers - replace if necessary
   - ? during injection, look for a tight, straight stream
   - ? make sure there is sufficient printer paper
   - ? check levels of standard solutions, deionized water, and acid - replenish as required

5. Clean the water delivery system. First, take the unit offline. To do this press start/stop. Two tabs will appear on the bottom of the screen. Press F-1 which should be associated with the stop tab. At this point the green light on the start/stop

6. key should go off. Next turn the main flow valve to the off position. Disconnect the "quick-connect" fittings below the flow meter and connect the system flush line to the "upstream" fitting. Turn the flow back on to flush any debris from the line. Allow it to keep running while you continue cleaning the system. Next, unscrew the top fitting on the flow meter (just above the transparent plastic piece). Scrub and run deionized water

through the flow meter and adjacent piping to clear debris. Disconnect the white tubing just upstream of the flow meter that carries flow to the autoanalyzer. Run deionized water through the white tubing and through the top of the gray pipe that the white tubing fits into until debris is removed. Reconnect tubing, flow meter and quick-connects. Turn water flow off prior to removing system flush line. At this point, the quicker the flow is restored, the cleaner the flow should be when online sampling is resumed.

7. Turn unit back online. To put autoanalyzer online, press return tab key, F-1, to get to main screen. "Online" tab should appear at left of screen over F-1; press it. To initiate online sampling, scan the screen that's in view to make sure correct condition # is selected (currently condition #3). If everything looks acceptable press start/stop to begin sampling. The green light in the start/stop key should illuminate.
8. While online sampling is running, collect QC grab samples from canal and spigot. Collect the canal samples with the extend-a-pole and stainless steel container near the pump intake prior to collecting spigot sample. This will allow the Shimadzu to run a while and clear out any debris left in the line from the cleaning process. When opening the spigot, let the water run for a short while to remove debris from the sample port and line. Make sure to rinse churn-splitter three times for both canal and spigot sample collections (something about the number of lab and grab sample to collect).
9. Once all lab and grab samples have been collected. Turn the autoanalyzer offline following the instructions provided prior. Set up the unit in grab sample mode. Turn the small flow valve on the left side of the Shimadzu from "online" to "grab" (make sure the arrow on the handle lines up with the markings on the unit or insufficient flows may occur). Set up the magnetic stirrer stand with one of the grab vials in place. Add a clean stir-bar to the sample and set the speed of the stirrer so as not tot create a vortex. Connect the grab sample port using "clean" procedures and place grab sample tube in the sample. Turn unit back online to start sampling. Repeat procedure for the next grab sample, making sure to rinse the outside of the grab sample tube and stir-bar with deionized water (and removing excess water) prior to beginning.
10. Once running of grab samples is complete, clean off all equipment and put away in proper place. Turn the small flow valve on left side of unit back to "online" (again, make sure arrow lines up). Follow earlier instructions for placing unit online.
11. Remove printout to take back to the office, do final check on flows, and watch at least one sample run on the unit to make sure that it is operating properly. Pick up area, turn off lights and lock the door on your way out.

1.2 <u>Monthly Site Visit</u>

1. **Sample Injection Condition**: The manner in which the sample is injected from the injection tube will greatly affects the repeatability and the precision of analyses. The injection condition should be examined monthly to insure that a symmetrical vertical stream is present; the stream is viewed through the combustion tube during normal operation. If the stream is asymmetrical or deflected change to the SERVICE screen and make the appropriate adjustment using the SAMPLE INJECTION CHECK item. It may be necessary to remove the tube for cleaning; if necessary, cut off about 1 mm of the tip of the tube with a razor blade, reattach and then verify that the injection is normal.

2. **Inspection and Cleaning of Combustion Tube**: Inspect the combustion tube for excessive whitening of the internal surface caused by buildup of salts and combustion products. If needed remove the tube and wash in HCl per manufacturers directions.
3. **Replacing CO_2 Absorber:** The CO_2 absorbers for cleaning carrier gas, for cleaning the NDIR optical system purge gas and for cleaning the sparge gas is replaced with a new canister once a month.
4. **Inspection and Replacement of Halogen Scrubber:** As the halogen scrubber absorbs chlorine, the absorbent darkens. Once the discoloration nears the exit end of the scrubber is must be replaced with a new scrubber. To increase service like, the acid additions during the DIC sparging process should be kept to a minimum. Under continuous operation the scrubber should be replaced every 6 months or earlier if excessive discoloration occurs. Note the membrane filter should also be replaced when a new scrubber is installed. See the Shimadzu 4100 operator manual for more information.
5. **Regenerating the Catalyst:** Various inorganic substances accumulate on the catalyst bed in the form of salts or oxidized substances and when accumulations become excessive instrument performance can be degraded and the catalyst should be regenerated. This service will typically only be needed if the instrument is operated in TC measurement mode rather than the standard NPOC mode because in NPOC mode the samples being injected into the combustion tube are already acidic and it is unlikely that catalyst degradation will occur. See the Shimadzu 4100 operator manual for more information.
6. **Inspection and Replacement of the Syringe Plunger Tip:** The plunger tip will gradually wear as it is used and eventually gaps will occur between the plunger tip and syringe barrel resulting in leakage. Leakage can be detected by bubbles forming near the plunger tip when sample is drawn or the sample will leak from the bottom of the barrel when it is injected from the syringe. See the Shimadzu 4100 operator manual for more information on tip replacement.